Photochemical versus Thermal Synthesis of Cobalt Oxyhydroxide Nanocrystals

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Abstract
Photochemical methods facilitate the generation, isolation, and study of metastable nanomaterials having unusual size, composition, and morphology. These harder-to-isolate and highly reactive phases, inaccessible using conventional high-temperature pyrolysis, are likely to possess enhanced and unprecedented chemical, electromagnetic, and catalytic properties. We report a fast, low-temperature and scalable photochemical route to synthesize very small (~3 nm) monodisperse cobalt oxyhydroxide (Co(O)OH) nanocrystals. This method uses readily and commercially available pentaamminechlorocobalt(III) chloride, [Co(NH₃)₅Cl]Cl₂, under acidic or neutral pH and proceeds under either near-UV (350 nm) or Vis (575 nm) illumination. Control experiments showed that the reaction proceeds at competent rates only in the presence of light, does not involve a free radical mechanism, is insensitive to O₂, and proceeds in two steps: (1) Aquation of [Co(NH₃)₅Cl]²⁺ to yield [Co(NH₃)₅(H₂O)]³⁺, followed by (2) slow photoinduced release of NH₃ from the aqua complex. This reaction is slow enough for Co(O)OH to form but fast enough so that nanocrystals are small (ca. 3 nm). The alternative dark thermal reaction proceeds much more slowly and produces much larger (~250 nm) polydisperse Co(O)OH aggregates. UV-Vis absorption measurements and ab initio calculations yield a Co(O)OH band gap of 1.7 eV. Fast thermal annealing of Co(O)OH nanocrystals leads to Co₃O₄ nanocrystals with overall retention of nanoparticle size and morphology. Thermogravimetric analysis shows that oxyhydroxide to mixed-oxide phase transition occurs at significantly lower temperatures (up to T = 64 degrees C) for small nanocrystals compared with the bulk.

Keywords
Ab initio calculations, Aqua complexes, Catalytic properties, control experiments, fast thermal annealing, free radical mechanism, high-temperature pyrolysis, low temperatures, monodisperse, nanoparticle sizes, neutral pH, Oxyhydroxides, Pentaamminechlorocobalt, Photochemical method, thermal synthesis, chlorine compounds, cobalt, cracking (chemical)

Disciplines
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Photochemical versus Thermal Synthesis of Cobalt Oxyhydroxide Nanocrystals

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ABSTRACT: Photochemical methods facilitate the generation, isolation, and study of metastable nanomaterials having unusual size, composition, and morphology. These harder-to-isolate and highly reactive phases, inaccessible using conventional high-temperature pyrolysis, are likely to possess enhanced and unprecedented chemical, electromagnetic, and catalytic properties. We report a fast, low-temperature and scalable photochemical route to synthesize very small (∼3 nm) monodisperse cobalt oxyhydroxide (Co(O)OH) nanocrystals. This method uses readily and commercially available pentaamminechlorocobalt(III) chloride, [Co(NH₃)₅Cl]Cl₂, under acidic or neutral pH and proceeds under either near-UV (350 nm) or Vis (575 nm) illumination. Control experiments showed that the reaction proceeds at competent rates only in the presence of light, does not involve a free radical mechanism, is insensitive to O₂, and proceeds in two steps: (1) Aquation of [Co(NH₃)₅Cl]Cl₂ to yield [Co(NH₃)₅(H₂O)]Cl³⁺, followed by (2) slow photoinduced release of NH₃ from the aqua complex. This reaction is slow enough for Co(O)OH to form but fast enough so that nanocrystals are small (ca. 3 nm). The alternative dark thermal reaction proceeds much more slowly and produces much larger (∼250 nm) polydisperse Co(O)OH aggregates. UV–Vis absorption measurements and ab initio calculations yield a Co(O)OH band gap of 1.7 eV. Fast thermal annealing of Co(O)OH nanocrystals leads to Co₃O₄ nanocrystals with overall retention of nanoparticle size and morphology. Thermogravimetric analysis shows that oxyhydroxide to mixed-oxide phase transition occurs at significantly lower temperatures (up to ΔT = 64 °C) for small nanocrystals compared with the bulk.

INTRODUCTION

Nanotechnology is rapidly evolving toward the fabrication of ever more complex heterostructured nanomaterials with precise morphology, composition, and properties.¹⁻³ Traditional nanomaterial syntheses rely heavily on thermal decomposition or “pyrolysis” of precursors in high-boiling solvents at high temperature, often in excess of 250–300 °C. Under such conditions, isolating highly reactive and unstable nanocrystal phases can be challenging. An example is doped nanocrystals, where the dopants or chemical “defects” sit within just a few lattice parameters from the nanocrystal surface and get easily thermally extruded, diffusing away in favor of a more stable homogeneous lattice under typical synthesis temperatures.⁴,⁵ These limitations severely narrow the range of metastable nanocrystalline phases that can be built through traditional high-temperature pyrolysis. This problem is of particular timeliness and relevance because it is harder to isolate the more reactive metastable phases that are most likely to possess enhanced magnetic, chemical, and catalytic properties and perhaps also unprecedented optoelectronic properties.

Photochemistry is regularly employed by molecular chemists to generate highly reactive species. Similarly, light may be an ideal tool for building metastable nanomaterials.⁶ Light-induced reactions usually proceed through alternate pathways at low temperature. Chalcogenide-based nanomaterials such as bismuth selenide nanocrystals⁷ and tellurium nanorods,⁸ which previously could not be prepared thermally (by simple heating), were recently prepared photochemically. Surface-bound platinum and palladium nanoparticles were selectively photodeposited along site-specific segments of axially graded semiconductor nanorods by carefully selecting the irradiation wavelength.⁹,¹⁰ Soluble gold nanoparticles¹¹ and gold nanorods¹² and oxides such as ceria nanocrystals¹³ were also prepared with the aid of light.

Cobalt oxyhydroxide (Co(O)OH), also referred to by its mineral name of “heterogenite”, is an example of a metastable phase that can be difficult to isolate on the nanoscale using conventional preparative methods. Co(O)OH is an active component in gas (CO) sensing and detection, oxygen evolution catalysts, and alkaline (Li) batteries.¹⁴ Isolating Co(O)OH requires stabilizing Co(III) against Co(II) under basic conditions while preventing formation of Co₂O₃; a common byproduct,¹⁵⁻¹⁷ or precipitation of cobalt hydroxides.¹⁸,¹⁹ Typical preparations involve treating Co(OH)₂ or...
other Co(II) source with an oxidant such as hydrogen peroxide (H₂O₂) or sodium hypochlorite (NaClO) at pH ~14.20–23 These thermal reactions are usually slow, taking up to 18 h at 45 °C or 6 h at 120 °C.14,20 They tend to produce large ca. 500 nm aggregates of clustered 20 nm × 20 nm hexagonal nanocrystals, although certain conditions yield isolated 120 nm × 120 nm hexagonal nanocrystals.24,25 Spatially constrained or sonication-assisted syntheses produce even larger Co(O)OH aggregates.24,25 Here we describe a room temperature (RT) photochemical synthesis of small ca. 3 nm Co(O)OH colloidal nanocrystals in as little as 2–4 h under either ultraviolet (UV) or visible (Vis) light irradiation. This method uses readily available precursors such as pentaamminechlorocobalt(III) chloride, [Co(NH₃)₅Cl]Cl₂, and whole-flask illumination with widely available fluorescence lamps. In contrast, we show that similar thermal reactions, run by heating the sample to 80 °C overnight, lead to larger 100–300 nm Co(O)OH aggregates. We present complete optical, structural, and computational characterization and modeling for Co(O)OH and use the photochemically and thermally produced nanocrystals as precursors for the synthesis of differently sized Co₃O₄ nanocrystals via thermal annealing.

### EXPERIMENTAL SECTION

#### Materials.

Co(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.999%), pentaamminechlorocobalt(III) chloride ([Co(NH₃)₅Cl]Cl₂, 98%), concentrated ammonium hydroxide (NH₄OH, ACS Reagent), and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 98%) were purchased from Aldrich. Hexaamminecobalt(III) chloride ([Co(NH₃)₆]Cl₃, 99.999%) was purchased from Strem. Sodium bicarbonate (NaHCO₃, ACS), concentrated nitric acid (HNO₃, ACSPlus), concentrated hydrochloric acid (HCl, ACSPlus), and hydrogen peroxide (H₂O₂, 30%) were purchased from Fisher. Pentaamminechlorocobalt(III) perchlorate, [Co(NH₃)₅Cl]ClO₄·2H₂O, is synthesized as previously reported.29 All chemicals were used as received unless specified otherwise.

#### Synthesis.

Co(O)OH Nanocrystals. Photochemical Synthesis. Pentaamminechlorocobalt(III) perchlorate, [Co(NH₃)₅Cl]ClO₄·2H₂O (30.8 mg, 81.4 μmol), or pentaamminechlorocobalt(III) chloride, [Co(NH₃)₅Cl]Cl₂ (41.5 mg, 166 μmol), was dissolved in 15 mL of either deionized water or 0.01 M aqueous HCl. The solution was added dropwise until pH 7.4. The resulting pink solution, containing [Co(H₂O)₆]³⁺ ions, was irradiated at 350 nm for 2 h.25

Hexaamminecobalt(III) chloride, [Co(NH₃)₆]Cl₃ (39.3 mg, 1.57 mmol), was dissolved in 15 mL of deionized water. This solution was irradiated at 350 nm for 2 h. The reaction mixture was centrifuged (4000 rpm × 5 min) to give dark-brown Co(O)OH powder.

Anaerobic Synthesis: Probing the Effect of O₂. Co(NH₃)₅Cl⁺Cl⁻ (40.1 mg, 1.601 mmol) was dissolved in 15 mL of deionized water. The solution was sparged with Ar for 15 min, sealed, and evacuated under dynamic vacuum for 3 min, then refilled with Ar, and the process was repeated three times. This solution was irradiated at 350 nm for 2 h.

Radical Trap Effect. [Co(NH₃)₅Cl]Cl₂ (39.3 mg, 1.57 mmol) was dissolved in 15 mL of deionized water. 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO, 55.3 mg, 0.354 mmol), was then added. The homogeneous solution was irradiated at 350 nm for 2 h. The reaction mixture was centrifuged (4000 rpm × 5 min) to give dark-brown Co(O)OH powder and an orange supernatant (soluble TEMPO).

Photolysis and Characterization. Photolyses utilized a fan-cooled Rayonet photoreactor with either 16 side-on 350 nm lamps (35 nm fwhm, intensity =136 W/m²) or 575 nm lamps (75 nm fwhm, intensity = 47.2 W/m²).

Absorption Spectroscopy. Ultraviolet–visible-near-infrared (UV–Vis-NIR) absorption spectra were recorded with a photodiode array Agilent 8453 spectrophotometer. Solvent absorption was subtracted from all spectra. We estimated the absorption coefficient of ca. 3 nm Co(O)OH nanocrystals to be e = 8.0 × 10⁶ M⁻¹cm⁻¹ at 680 nm (1.82 eV) and e = 1.6 × 10⁶ M⁻¹cm⁻¹ at 360 nm (3.44 eV).

X-ray Diffraction. Powder X-ray diffraction (XRD) data were measured using a Scintag XDS-2000 diffractometer equipped with a theta–theta goniometer, a sealed-tube solid-state generator providing Cu Kα radiation, and an air-cooled Kevex Psi Peltier silicon detector.

Transition Electron Microscopy (TEM). TEM was conducted on carbon-coated copper grids using a FEI Tecnai G2 F20 field-emission scanning transmission electron microscope (STEM) at 200 kV. Elemental composition was characterized by energy-dispersive spectroscopy (EDS) in STEM mode.

Thermogravimetric Analysis (TGA). TGA was conducted on a TA Instruments 2950 TGA at ISU’s Materials Analysis

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Research Laboratory. The sample was heated in N₂ to 520 °C at a rate of 20 °C/min and at a resolution of 5.0 °C.

**Computational Details.** Computations were completed on the CRUNCH system supported by the Computation Advisory Committee of Iowa State University. Band gaps were determined by calculating the DOS diagram and band structure using the Vienna ab initio simulation package (VASP). Projector-augmented wave (PAW) pseudopotentials and the Perdew–Burke–Ernzerhoff (PBE) generalized gradient approximation (GGA) were used. A Monkhorst-Pack k-points grid of 12 × 12 × 4 was used to sample the first Brillouin zone for reciprocal space integration. We utilized the GGA+U method to describe better the experimentally observed band gap. We determined that a value of $U = 3.2$ eV gave the best agreement with experiment.

**RESULTS AND DISCUSSION**

Photochemical Decomposition of [Co(NH₃)₅Cl]X₂ (X = Cl, ClO₄). As part of our studies of energy transfer between photoactive nanocrystals and transition metal complexes, we observed that irradiating aqueous solutions containing pentaamminechlorocobalt(III) ions with 350 nm light at 21–24 °C (RT) and pH 2 (acidified with 0.01 M HCl or HClO₄) for 3 h results in the formation of cobalt oxyhydroxide (Co(O)OH) nanocrystals. Pentaamminechlorocobalt(III), [Co(NH₃)₅Cl]²⁺, is a purple-colored water-soluble complex ion characterized by two absorption maxima ($\lambda_{\text{max}}$) at 355 and 525 nm (Figure 1). After 350 nm irradiation for 35 min, aqueous solutions of [Co(NH₃)₅Cl]²⁺ become brown, with two new, very intense bands appearing at 360 ($\lambda_{\text{max}}$) and 650 nm (shoulder). After 350 nm irradiation for 70 min, the initial absorption peaks from [Co(NH₃)₅Cl]²⁺ are no longer visible. Centrifugation of this solution results in the separation of a brown powder that can be resuspended in methanol. The pH of the supernatant is 8.8. We later observed that the brown powder, which consists of nanocrystalline Co(O)OH (see below), also forms when 575 nm light is used and even when the reaction is run in the absence of acid, in which case the initial solution pH is 6.5 while the supernatant pH is 8.8.

Powder XRD shows that the brown precipitate consists of crystalline cobalt oxyhydroxide, Co(O)OH (Figure 2). Cobalt oxyhydroxide crystallizes in a hexagonal unit cell with lattice parameters $a = 2.855$ Å and $c = 8.805$ Å. The structure consists of anionic [CoO]⁻ layers of Co³⁺ ions, each octahedrally coordinated by triply bridging oxide ligands ($\mu_{3}$-O²⁻); [CoO]⁻ layers are held together by hydrogen bonds, with each H⁺ ion bridging together two oxides from adjacent layers.

![Figure 1. UV–Vis absorption spectra of thermal and photochemical Co(O)OH in methanol and of [Co(NH₃)₃(OH₂)]Cl₂, [Co(NH₃)₅(OH₂)]Cl₃, and Co₃O₄ in water.](image1)

![Figure 2. XRD data for: Photochemically prepared Co(O)OH (a), thermally prepared Co(O)OH (b), bulk Co(O)OH (c), Co₃O₄ made by thermal annealing of photochemically prepared Co(O)OH (d), Co₃O₄ made by thermal annealing of thermally prepared Co(O)OH (e), and bulk Co₃O₄ (f).](image2)

![Figure 3. Crystalline structure of Co(O)OH viewed down the y axis (a) and z axis (b) (gray = Co; red = O; white = H).](image3)
fringes in all nanocrystals, and selected area diffraction (SAD) patterns show spacings of 0.45 (003), 0.24, 0.22 (102), and 0.21 nm (006), each of which is in close agreement with the spacings observed in the powder XRD pattern (Figure 1). Energy-dispersive X-ray diffraction (EDS) area scans confirm the presence of both cobalt and oxygen.

Thermal Decomposition of \([\text{Co(NH}_3\text{)}_5\text{Cl}]_2\text{X}_2\) (X = Cl, ClO_4). To probe the role of light in the formation of cobalt oxyhydroxide, we carried out several thermal syntheses and mechanistic control experiments (see below). Aqueous solutions containing pentaamminechlorocobalt(III), \([\text{Co(NH}_3\text{)}_5\text{Cl}]^2+\), kept in the dark at 21−24 °C (RT), show no appreciable particle formation for over 4 days (>96 h). Similarly, heating aqueous solutions containing \([\text{Co(NH}_3\text{)}_5\text{Cl}]^2+\) to 80 °C at pH 2 (acidified with HCl) in the dark for 24 h does not form cobalt oxyhydroxide, Co(O)OH, but likely the aquation product, pentaammineaquacobalt(III), \([\text{Co(NH}_3\text{)}_5(\text{OH}_2)]^3+\). UV−Vis spectra show a blue-shift of λ_max values from 355 nm and 525 nm to 305 nm and 509 nm, respectively (Figure 1, see below). However, heating aqueous solutions containing pentaamminechlorocobalt(III), \([\text{Co(NH}_3\text{)}_5\text{Cl}]^2+\), ions at 80 °C and pH 6.5 (near-neutral pH without acid or base added) in the dark for 24 h results in the formation of brown-colored Co(O)OH, as determined from XRD (Figure 2). The UV−Vis absorption spectrum of this thermally prepared Co(O)OH shows two intense bands at 410 (λ_max) and 710 nm (shoulder), which are red-shifted compared with the photochemically prepared Co(O)OH (Figure 1). After separation of the brown precipitate by centrifugation, the colorless supernatant has a pH of 9.1 and is completely transparent in the 300−1100 nm spectral region. However, in contrast with the small and highly crystalline nature of the photochemically produced Co(O)OH, TEM micrographs show the thermally prepared Co(O)OH consists of large aggregates of 70 nm × 10 nm crystalline rods embedded within larger ca. 250 nm amorphous flake-like regions (Table 1, Figure 5).

Table 1. Synthesis of Co(O)OH and Co_3O_4 Nanocrystals under Different Conditions

<table>
<thead>
<tr>
<th>no.</th>
<th>precursor</th>
<th>conditions</th>
<th>product</th>
<th>TEM particle size/ nm</th>
<th>XRD particle size/ nm^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Co(NH}_3\text{)}_5\text{Cl}]_2\text{X}_2) (X = Cl, ClO_4)</td>
<td>photochemical (350 nm or 575 nm), 2 &lt; pH &lt; 6.5 (aqueous)^a</td>
<td>Co(O)OH (1.9 eV)^c</td>
<td>3.3 ± 0.9</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Co(NH}_3\text{)}_5\text{Cl}]_2\text{X}_2) (X = Cl, ClO_4)</td>
<td>thermal (80 °C, in the dark, pH = 6.5 (aqueous)^a</td>
<td>Co(O)OH (1.7 eV)^c</td>
<td>ca. 250 (aggregates)</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>Co(O)OH (photo 3.3 nm)</td>
<td>annealing at 250 °C, 30 min (dry)</td>
<td>Co_3O_4</td>
<td>5.0 ± 1.0</td>
<td>3.8</td>
</tr>
<tr>
<td>4</td>
<td>Co(O)OH (thermal 250 nm)</td>
<td>annealing at 280 °C, 40 min (dry)</td>
<td>Co_3O_4</td>
<td>ca. 125 (aggregates)</td>
<td>39</td>
</tr>
</tbody>
</table>

^a[Co]_total = 0.01 M. ^bCalculated from XRD peak widths using Scherrer equation. ^cObserved absorption onset.

Figure 4. Representative TEM (a), selected area diffraction (SAD) (b), and high-resolution (HR) TEM (c) of photochemically prepared Co(O)OH nanocrystals. Representative TEM (d) of Co_3O_4 prepared by thermal-annealing of photochemically prepared Co(O)OH. Particle size histograms of photochemically prepared Co(O)OH (e) and Co_3O_4 prepared by thermal-annealing of photochemically prepared Co(O)OH (f).

Figure 5. TEM of thermally prepared Co(O)OH nanocrystals (approximate size of the rod-like structures is 70 nm × 10 nm) (a) and Co_3O_4 nanocrystals prepared by thermal-annealing of thermally prepared Co(O)OH (approximate size of rod-like structures is 30 nm × 3 nm) (b).
Mechanistic and Control Experiments. To gain a better understanding on the formation mechanism of Co(O)OH nanocrystals, we subjected several starting materials to different reaction conditions. Because cobalt oxyhydroxide (Co(O)OH) features Co$^{3+}$ ions in an all-oxygen coordination environment, we considered the possibility that its formation could involve a cobalt-hexaaqua, [Co(OH$_2$)$_6$]$^{3+}$, complex intermediate. We irradiated hexaaquacobalt(III), [Co(OH$_2$)$_6$]$^{3+}$, solutions at 350 nm under acidic pH (1 < pH < 2). Irradiation of the deep-blue [Co(OH$_2$)$_3$]$^{2+}$, with $\lambda_{max}$ at 400 nm and 605 nm, leads in 1 h to the formation of the light-pink hexaaquacobalt(II), [Co(OH$_2$)$_5$]$^{2+}$, with $\lambda_{max}$ at 510 nm$^{25,36,37}$ but no Co(O)OH (entry 1 in Table 2, Figure 6). Repeating this procedure six times, for a total irradiation time of 16 h, the supernatant was then irradiated again for 4 h. This procedure was repeated four times, for a total irradiation time of 16 h. The resulting series of spectra obtained for the supernatant solution was then repeated, and the absorption of the supernatant recorded. The supernatant was then centrifuged, the formed Co(O)OH precipitate was removed, starting at pH 6.5. Every 4 h, the reaction mixture was centrifuged, the formed Co(O)OH precipitate was removed, and the absorption of the supernatant recorded. The supernatant was then irradiated again for 4 h. This procedure was repeated four times, for a total irradiation time of 16 h. The resulting series of spectra obtained for the supernatant solution show that the initial [Co(NH$_3$)$_5$Cl]$^{2+}$ ion is first transformed to the aquation product, [Co(NH$_3$)$_5$(H$_2$O)]$^{3+}$, in under 4 h, as evidenced by a blue shift in $\lambda_{max}$ from 525 to 509 nm, respectively (Figures 1 and 7). The estimated apparent rate of reaction is <0.4 mM/h with a first half-life of ~9 h.

Computational Modeling. We used the Vienna ab initio simulation package, VASP v. 4.6, and the GGA+U method with PBE pseudopotentials to model and estimate the bulk bandgap of cobalt oxyhydroxide, Co(O)OH. We implemented a Hubbard U parameter$^{48}$ to better describe the localization of the electrons around the Co$^{3+}$ ions and thus provide a realistic band gap. The GGA+U method provided an accurate description of the band gap in Co$_3$O$_4$. Previous quantum chemical modeling yielded a Co(O)OH band gap of 1 eV.$^{46}$ A DOS diagram computed using $U = 3.2$ eV shows a band gap of ~1.7 eV (Figure 8). This is a close fit with our experimental absorption data for thermally prepared Co(O)OH nanocrystals, which show a first absorption peak at ~710 nm (1.7 eV) (Figure 1). In contrast, photochemically prepared
Co(O)OH nanocrystals show a significantly bluer first absorption peak (shoulder) at \( \lambda_{\text{max}} \approx 650 \text{ nm} \) (1.9 eV). Because the average single crystal domain (grain) size obtained from XRD for thermally prepared Co(O)OH (ca. 17 nm, Table 1) is significantly larger than that for photochemically prepared Co(O)OH (ca. 3 nm, Table 1), we conclude that there is some degree of quantum confinement in the latter. Using only GGA-PBE yielded a band gap of 0.6 eV (2,067 nm). Adding \( U = 1.0 \text{ eV} \) gave a band gap of ca. 1.0 eV (1240 nm), whereas a value of \( U = 4.0 \text{ eV} \) gave an unrealistically large band gap of 2.0 eV (620 nm). The partial DOS diagram shows that the d orbital splitting in Co\(^{3+}\) is the source of this band gap (Figure 8).

**Thermal Analysis.** We used TGA to probe the temperature-induced mass loss of photochemically and thermally prepared Co(O)OH (Figure 9). In both cases, plots of mass loss versus temperature show a major change corresponding to the phase transition from cobalt oxyhydroxide to mixed-cobalt(II,III) oxide: 12Co(O)OH \( \rightarrow \) 4Co\(_3\)O\(_4\) + 6H\(_2\)O + O\(_2\). \(^{14}\) Interestingly, this transition occurs at significantly lower temperature for photochemically prepared Co(O)OH, 206 °C, than for thermally prepared Co(O)OH, 251 °C. In the bulk, the reported transition temperature is even higher, 258–270 °C. We attribute this significant drop in phase transition temperature to a sharp decrease in the amount of heat needed to phase transform very small ca. 3 nm (photochemical) Co(O)OH nanocrystallites to Co\(_3\)O\(_4\) compared with larger ca. 250 nm (thermal) nanocrystallites or bulk Co(O)OH (Table 1, Figure 9). \(^{47–52}\)

**Preparative Transformation of Co(O)OH into Co\(_3\)O\(_4\) Nanocrystals.** On the basis of our TGA analysis, we explored the synthetic utility of Co(O)OH in making Co\(_3\)O\(_4\) nanocrystals. \(^{14,20,53–55}\) Heating the photochemically prepared Co(O)OH to 250 °C for 30 min or the thermally prepared Co(O)OH to 280 °C for 30 min leads to the formation of cobalt(II,III) oxide, Co\(_3\)O\(_4\), as confirmed by UV–Vis and XRD. In both cases, the UV–Vis spectrum of the annealed product is significantly redshifted compared with the starting material, with new \( \lambda_{\text{max}} \) appearing at 400 nm (3.1 eV) and 750 nm (1.7 eV) (Figure 1). The reddest peak (band onset) is not far from the literature band gap of 1.5 eV (827 nm), \(^{56}\) and is visually manifested by a color change from brown for Co(O)OH to very dark/off-gray for Co\(_3\)O\(_4\). The powder XRD pattern of the annealed samples shows the disappearance of the major Co(O)OH peak at 2\( \theta \) = 20° and the appearance of a smaller Co\(_3\)O\(_4\) peak at 2\( \theta \) = 18° (Figure 2). Co\(_3\)O\(_4\) has a spinel structure (lattice parameter \( a \approx 8.08 \text{ Å} \)) made of cubic close-packed O\(^{2−}\) ions with Co\(^{2+}\) and Co\(^{3+}\) ions in tetrahedral and Co\(^{3+}\) octahedral holes, respectively. Interestingly, TEM micrographs of Co\(_3\)O\(_4\) nanocrystals reveal a similar size, morphology, and level of aggregation compared with the Co(O)OH starting materials. \(^{14,56}\) Co\(_3\)O\(_4\) nanocrystals obtained from annealing the photochemically prepared Co(O)OH nanocrystallites are very small, 5.0 nm \( \pm \) 1.0 nm (Table 1, Figure 5). To the best of our knowledge, this is one of the smallest sizes reported for free Co\(_3\)O\(_4\) nanocrystallites in the literature. \(^{57}\) In contrast, TEM micrographs of Co\(_3\)O\(_4\) nano-
crystals obtained from annealing the thermally prepared Co(O)OH nanocrystals show the presence of 30 nm × 3 nm crystalline rods embedded within larger ca. 150 nm aggregates (Figure 5 and Table 1). The morphologies observed by TEM correlate with the relative crystalline domains (grain sizes) of ca. 3.8 nm (photochemical Co(O)OH precursor) and ca. 39 nm (thermal Co(O)OH precursor) for Co3O4 nanocrystals obtained from XRD peak widths (Table 1).35 Therefore, the size and morphology of Co(O)OH starting material controls to a significant extent the size and morphology of the Co3O4 product.58–61 Similar transformations starting from Co(O)OH may be useful in the fabrication of lithium storage materials such as lithium cobalt oxide, LiCoO2.62

## CONCLUSIONS

In summary, we found a fast, low-temperature and scalable photochemical route to synthesize very small (~3 nm) monodisperse cobalt oxyhydroxide (Co(O)OH) nanocrystals. This method uses readily and commercially available [Co(NH3)5Cl]2+ under acidic or neutral pH and proceeds under either near-UV (350 nm) or Vis (575 nm) lamp illumination. Control experiments showed that the reaction proceeds at competent rates only in the presence of light, does not involve a free radical mechanism, is insensitive to O2 from air, and proceeds via two steps: (1) Aquation of [Co(NH3)5Cl]2+ to yield [Co(NH3)5(H2O)]2+, followed by (2) slow, autocatalytic release of NH3 from this complex. This reaction is slow enough for Co(O)OH to form but fast enough so that nanocrystals are small (ca. 3 nm). The alternative dark thermal reaction proceeds much more slowly and produces much larger (~250 nm) polydispersed Co(O)OH aggregates. UV–Vis absorption measurements and ab initio calculations yielded a Co(O)OH band gap of 1.7 eV. Fast thermal annealing of Co(O)OH nanocrystals leads to Co3O4 nanocrystals with overall retention of nanoparticle size and morphology. TGA showed that the oxyhydroxide to mixed-oxide phase transition occurs at significantly lower temperatures (up to ΔT = 64 °C) for small nanocrystals compared with the bulk material. We expect that the use of similar photochemical methods will permit the generation, isolation, and study of other metastable nanomaterials of unusual size, composition, and morphology. These harder-to-isolate and highly reactive phases, inaccessible using conventional high-temperature pyrolysis, are likely to possess enhanced and unprecedented chemical, electromagnetic, and catalytic properties.

## ASSOCIATED CONTENT

* Supporting Information Additional HRTEM and SAED data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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